

Chemistry A European Journal



European Chemical Societies Publishing

Accepted Article

Title: Supramolecular Paradigm for Capture and Co-Precipitation of Gold(III) Coordination Complexes

Authors: Bradley D. Smith, Cassandra C. Shaffer, Wenqi Liu, and Allen G. Oliver

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Chem. Eur. J. 10.1002/chem.202003680

Link to VoR: https://doi.org/10.1002/chem.202003680



Supramolecular Paradigm for Capture and Co-Precipitation of Gold(III) Coordination Complexes

Cassandra C. Shaffer, Wenqi Liu, Allen G. Oliver, and Bradley D. Smith*

Abstract: A new supramolecular paradigm is presented for reliable capture and co-precipitation of haloauric acids (HAuX₄) from organic solvents or water. Two classes of acyclic organic compounds act as complementary receptors (tectons) by forming two sets of directional non-covalent interactions, (a) hydrogen bonding between amide (or amidinium) NH residues and the electronegative X ligands on the AuX4⁻, and (b) electrostatic stacking of the electron deficient Au center against the face of an aromatic surface. X-ray diffraction analysis of four co-crystal structures reveals the additional common feature of proton bridged carbonyls as a new and predictable supramolecular design element that creates one-dimensional polymers linked by very short hydrogen bonds (CO···OC distance < 2.5 Å). Two other cocrystal structures show that the amidinium- $\pi\cdots XAu$ interaction will reliably engage AuX4- with high directionality. These acyclic compounds are very attractive as co-precipitation agents within new "green" gold recovery processes. They also have high potential as tectons for controlled self-assembly or co-crystal engineering of haloaurate composites. More generally, the supramolecular paradigm will facilitate the design of next-generation receptors or tectons with high affinity for precious metal square planar coordination complexes for use in advanced materials, nanotechnology, or medicine.

Introduction

Not only is gold a common precious metal in jewels and coins, it is also employed increasingly within modern industries such as telecommunications, nanotechnology, chemical synthesis, and medicine. As a result, world demand for gold continues to increase which raises interest in developing new methods of extracting it from the earth or recovering it from societal waste streams.^{[1] [2]} In addition, there is a growing need for advanced materials that are comprised of gold containing nanocomposites with nanoscale architecture.^{[3] [4]} A rational, bottom-up synthesis of these nanocomposites has the attraction of precise atomiclevel control, but successful implementation requires selfassembly paradigms that can produce predictable lattices and super structures. In addition to the impressive advances in controlled assembly of elemental gold, [4] [5] there is a scattered body of work on self-assembly and crystal engineering of gold coordination complexes. Most success has involved twocoordinate Au(I) complexes which are known to regularly engage in Au…Au and Au… π interactions that promote formation of continuous atomic networks.^{[6] [7] [8]} At present, programmed self-

 C. C. Shaffer, Dr. W. Liu, Dr. A. G. Oliver, Dr. B. D. Smith Department of Chemistry & Biochemistry University of Notre Dame
 236 Nieuwland Science Hall, University of Notre Dame, IN., 46545, USA. Email: smith.115@nd.edu

Supporting information for this article is given via a link at the end of the document

assembly of four-coordinate Au(III) complexes is harder to control because the aurophilic interactions are inherently weaker.^[8] There is a particular need for new self-assembly methods that capture and immobilize industrially important Au(III) compounds such as chloroauric (HAuCl₄) or bromoauric (HAuBr₄) acid which can be produced from ores and waste streams by straightforward processes.^[9] Emerging research suggests that "areen" haloaurate recovery methods can be developed by applying modern supramolecular improvements to large scale extraction or co-precipitation technologies.^[10] Similarly, effective methods for precise supramolecular recognition of haloaurate complexes are likely to spur new approaches to core/shell gold nanoaprticles,^[11] spatially immobilized catalytic gold,^[12] or controlled delivery of medicinal gold.^[13] Common to these potential applications are supramolecular strategies that treat anionic square planar AuX4⁻ complexes as guest molecules or building blocks (tectons),[14] with distinctive sizes, shapes and electrostatic surfaces. In recent years, a number of macrocyclic host molecules, such as α -cyclodextrin,^[15,16] cucurbiturils,^{[17] [18]} ^[19] and cationic cyclophanes,^[20] have been reported as additives that can induce co-precipitation of specific haloaurate salts. X-ray





Counter cation: C=O····H⁺···O=C (very rare)

Scheme 1. Side-view of square planar AuX₄⁻ associated with macrocyclic (top) or acyclic (bottom) compounds. Two sets of directional non-covalent interactions (hydrogen bonding and Au aromatic stacking) are central to the supramolecular paradigm.

FULL PAPER



Scheme 2. Synthesis of compounds 1 - 5.

diffraction analysis of crystals from these co-precipitates has revealed intricate networks of weakly attractive interactions such as CH····XAu hydrogen bonds and ion-dipole interactions, and in some cases hydrogen bonding with coordinated water molecules. But the general picture from these crystal structures indicates no common set of relatively strong, directional non-covalent interactions that can be exploited to reliably induce a specific super structure or lattice assembly.

Recently, our group reported that tetralactam macrocycles, such as the structure shown in Scheme 1, were capable of coprecipitating square planar complexes of $MX_4^{\cdot n}$, where M = Au, Pd, Pt and X = Cl, Br from organic solution.^[21] X-ray crystal structures of the co-precipitated complexes showed that, in each case, the square planar $MX_4^{\cdot n}$ was encapsulated inside the macrocyclic cavity. Present in each structure were two key non-covalent interactions, (a) hydrogen bonding between the inward-directed amide NH residues of the macrocycle and the electronegative X ligands on the $MX_4^{\cdot n}$, and (b) electrostatic attraction between the two π -electron rich aromatic sidewalls of the macrocycle and the electron deficient central $M.^{[22]}$ We decided that a successful transition towards practical applications required a move away from organic macrocycles and towards

acyclic tectons that were easier to prepare on a large scale and more amenable to conjugation. We hypothesized that effective acyclic tectons must contain a combination of amide NH residues for strong directional hydrogen bonding to the X ligands of AuX₄and a π-electron rich aromatic surface to stack against the Au center (Scheme 1).^[23] Moreover, we reasoned that acyclic tectons based on the readily available starting compound, 1,4bis(aminomethyl)durene (BAMD),^{[21] [24]} would produce suitably preorganized molecular shapes that were complementary receptors for square planar AuX4-. Here, we report evidence that strongly supports our hypothesis by disclosing three new acyclic tectons that are very effective as co-precipitation compounds for haloauric acids. We describe a series of six co-crystal structures that each show hydrogen bonding and aromatic stacking as reliable drivers of the haloauric acid phase transfer and solid-state assembly. In addition, the crystal structures reveal two new types of non-covalent interactions that further facilitate the rational design of receptors or tectons for co-precipitation, nanocomposite self-assembly, or crystal engineering of haloauric acids.

Results and Discussion

The two symmetrical bis(amides) **1** and **2**, and the unsymmetric structure **5**, were each prepared from **BAMD** using straightforward synthetic chemistry (Scheme 2). The first set of co-precipitation experiments mixed HAuX₄ in dibutyl carbitol (a common industrial organic solvent used often for gold extraction^[25]) with a molar equivalent of the symmetrical compounds **1** or **2**. Small-scale gold recovery experiments were conducted using gravimetric analysis as detailed in the experimental section. Co-precipitation of the gold occurred almost instantaneously with > 85% recovery (Figure 1).



Figure 1. Illustration of typical co-precipitation experiment.

Recrystallization of the co-precipitates yielded single crystals that were suitable for analysis by X-ray diffraction. Shown in Figure 2 are illustrations of four separate solid-state structures; pure 1, $1 \cdot HAuCl_4$, $1 \cdot HAuBr_4$, $2 \cdot HAuCl_4$, and $2 \cdot HAuBr$. In the crystal-state, pure 1 adopts a slipped stacking motif in which each

FULL PAPER



Figure 2 X-ray crystal structures of pure 1, 1•HAuCl₄, 1•HAuBr₄, 2•HAuCl₄, and 2•HAuBr₄. The red oval highlights a "proton bridged carbonyls" motif (CO···H⁺···OC). For improved clarity, disorder is removed and there is inexact stoichiometry.

amide NH residue forms an intermolecular hydrogen bond with the carbonyl oxygen of an adjacent molecule. The crystal structures of 1•HAuCl₄ and 1•HAuBr₄ are very similar to each other, with the two amide groups on the same durene ring directed in opposite directions each forming a hydrogen bond with a stacked tetrahaloaurate anion. The resulting lattice is a continuous alternating stack of tetrahaloaurate anions and durene rings. For the 1•HAuCl₄ complex, the average NH···ClAu distance is 2.97 Å; whereas, in the case of **1**•HAuBr₄ the average NH…BrAu distance is 3.04 Å (the values refer to the H…X distance, see Table S1 for further details about these hydrogen bonds). The separation between parallel stacked durene rings is 7.069(3) Å for 1•HAuCl₄ and 7.293(3) Å for 1•HAuBr₄. Thus, compound 1 can form a co-crystal with AuCl4⁻ or the larger AuBr4⁻ without any major change in molecular conformation. This is not case with compound 2 which has two longer hexamide chains appended to a durene ring. The structure of 2-HAuBr₄ is very similar to those of 1•HAuX₄ with the two amide groups directed in opposite directions, but in the case of 2-HAuCl₄ both amide groups are directed to the same face of the common durene ring and the lattice packing is altered to accommodates this significantly very molecular shape. We attribute the change in solid-state molecular conformation to small differences in crystal packing energies caused by the size difference of AuCl₄ and AuBr₄. Overall, the four X-ray structures in Figure 1 confirm our hypothesis that the hydrogen bonding and aromatic stacking motifs shown in Scheme 1 are dominant intermolecular interactions that reliably drive co-precipitation and co-crystal crystal structure.[26]

An intriguing aspect with these four haloauric acid co-crystal structures is the location of the H^+ counter cation. Our previous work on co-crystals that included tetralactam macrocycles

consistently found a repeating lattice of macrocycle/haloaurate pairs bridged by a hydrated hydronium cation, a relatively common lattice location for H^{+, [21,27]} In striking contrast, a common feature of the four co-crystal structures in Figure 2 is a naked H⁺ bridging the carbonyls of adjacent tectons (Figure 3). In each case, this bridging proton was located in the Fourier difference map and further refined as described in the Supporting Information. The proton bridge creates a series of a linear, onedimensional polymers that stack to form sheets (Figures S23-S26) that in turn are layered to create the three dimensional lattice. Though uncommon, there are examples of proton bridged amide carbonyls in the crystal structure literature. [27] [28] [29] [30] [31] A recent computational modeling study by Love and coworkers proposed this motif as part of a supramolecular complex that formed when HAuCl4⁻ was extracted by a simple primary amide compound into an organic liquid phase,[32] and it was observed

X ₃ Au [¯] —X、 H			[−] X−AuX ₃
	C=O	C-N	CO…OC
1	1.236(2)	1.336(2)	-
1 ⋅HAuCl₄	1.268(2)	1.313(2)	2.428(2)
1 ∙HAuBr₄	1.270(3)	1.309(2)	2.423(2)
2·HAuCl ₄	1.272(6)	1.305(6)	2.437(3)
2 ∙HAuBr₄	1.278(4)	1.310(5)	2.441(4)

Figure 3. Selected average crystal structure bond lengths (Å).

FULL PAPER

WILEY-VCH



Figure 4. X-ray co-crystal structures of 5+HAuCl₄ and 5+HAuBr₄, along with a schematic picture of the structures. Disorder removed for clarity.

within the X-ray structure of an analogous [SnCl₆]²⁻ complex.^[31] It is notable that the four co-crystal structures containing bis(acetamide) 1 and bis(hexamide) 2 exhibit large differences in solid state packing due to changes in molecular size and shape, but in all cases the proton bridged amide carbonyl motif is maintained indicating it is a very robust and reliable packing interaction. Provided in Figure 3 is a comparison of bond distances for the amide groups in each of the four co-crystal structures as well as the crystal structure of pure bis(acetamide) 1. The average C=O bond length for the co-crystals is 1.272(8) Å, which is significantly longer than the 1.236(2) Å for pure 1; likewise, the average C-N bond length for the co-crystals is 1.308(9) Å, which is shorter than the 1.336(2) Å for pure 1. These bond differences suggest that the amide groups in each of the cocrystal structures have a higher fraction of the dipolar resonance contributor (confirmed by comparing differences in the calculated Mulliken charge distribution; see, Figure S37). The enhanced amide polarization in the co-crystal structures is due to cooperative hydrogen bonding with H^{+} at one end and AuX₄⁻ and the other end.^[33,34] Thus, the co-crystals can be considered as packed arrays of repeating [H⁺···amide···AuX₄⁻···amide···] units. Another noteworthy fact in Figure 3 is the extremely short average distance between proton bridged carbonyl oxygens which is 2.432(6) Å. Historically, a CO…OC distance < 2.5 Å has been called a short or low-barrier hydrogen bond, and there is considerable evidence that the free energy of formation in the solid state is in the range of -15 to -40 kcal mol⁻¹.[35] [36] At present, short hydrogen bonds are not rationally incorporated into the designs of supramolecular materials, but the results shown in Figures 2 and 3 highlight the usefulness of haloauric acids as a source of "anhydrous H⁺" to induce the proton bridged carbonyl motif.^[29,37,38] A recent study demonstrated that the motif persists in the solution state;^[27] thus, it seems plausible that bis(amides) like 1 and 2 can be employed to produce new classes of selfassembled polymers with "proton bridged carbonyls" as a reversible linker with very high bond strength.^[39]

Although it is conceivable that compounds 1 and 2 could be used practically for co-precipitation of haloauric acids from organic solvents, we felt that co-precipitation from water was likely to be more valuable as a potential gold recovery process.^[40] Thus, we synthetically substituted one of the neutral acetamide groups in symmetrical **1** with an isosteric, cationic acetamidinium group to create unsymmetrical compound **5** (Scheme 2). Co-precipitation experiments added an equimolar amount of **5** to separate aqueous solutions of HAuCl₄ or HAuBr₄ and in each case a co-precipitate formed instantly with >85% recovery by gravimetric analysis. Essentially identical co-precipitation results were obtained with HAuCl₄ in 0.1 M HCl, and subsequent treatment of solid **5**•HAuCl₄ with Na₂S₂O₅ or N₂H₂ produced gold metal as a precipitate leaving **5** in the filtrate for recrystallization and recycling.

Recrystallization of **5**•HAuCl₄ and **5**•HAuBr₄ yielded single crystals that were suitable for analysis by X-ray diffraction. Shown in Figure 4 is a representation of each crystal structure along with a schematic picture indicating the major non-covalent interactions. Consistent with our supramolecular paradigm, each AuX₄⁻ in the crystal was stacked between two aromatic durene rings and the peripheral X ligands on the square planar AuX₄⁻ formed a network of hydrogen bonds with amide and amindinium NH residues.^[26] In addition, the X ligands were in close contact with the methyl CH residues on an adjacent molecule and also with the electron-deficient π -orbital of an amidinium group on a second adjacent molecule. The latter contact is especially interesting; although Lewis acid/base interactions between electron rich ligands on metal complexes and π -acids are well



Figure 5. Amidinium group as L-shaped heteroditopic tecton that simultaneously forms directional amidinium-NH···XAu and amidinium- π ···XAu interactions oriented at about 90°.

documented,^[41] Au-X···π interactions are quite rare.^[8] ^[20] ^[23] Moreover, each amidinium group in Figure 4 acts as a heteroditopic L-shaped bridge that simultaneously engages one AuX₄⁻ by an amidinium-NH····XAu interaction and a second AuX₄⁻ by an amidinium- π ····XAu interaction with the vectors of the two non-covalent interaction oriented at about 90° (Figure 5). ^[26] Like the structures described above, the lattice packing for **5**-HAuCl₄ and **5**-HAuBr₄ can be viewed as a stack of one-dimensional polymers, this time in a zig-zag orientation with each tecton connected by a hydrogen bond between an amidinium-NH and an amide carbonyl oxygen on an adjacent molecule (Figures S27-S30). This hydrogen bonded polymer network promotes the selfassembly and co-crystallization processes.

Conclusions

The results of this study strongly support a new supramolecular paradigm for reliable capture and co-precipitation of HAuX₄ from organic solvents or water. Two families of acyclic organic compounds were designed to act as complementary supramolecular receptors (tectons) for HAuX4. They all induce coprecipitation of HAuX₄ by providing a combination of amide (or amidinium) NH residues for hydrogen bonding to the X ligands of AuX₄⁻ and a π -electron rich aromatic surface to stack against the electron-deficient Au center (Scheme 1).[22] X-ray diffraction analysis of four co-crystal structures that include bis(amides) 1 or 2 show the additional common feature of proton bridged carbonyls (CO···H+···OC) as a new way to create linear supramolecular polymers with very high hydrogen bond strength. Likewise, two co-crystal structures that include the unsymmetrical amidinium 5 reveal lattice packing of linear hydrogen bonded polymers. In addition, the amidinium- π ···XAu interaction is observed as a new L-shaped heteroditopic tecton with high directionality. The convenient synthesis of these acyclic compounds, or their conjugates, makes them very attractive for incorporation within "green" gold recovery processes. Furthermore, they have high potential as tectons for controlled self-assembly or co-crystal engineering of composites containing HAuX₄. Equally important, the underlying supramolecular paradigm can be exploited as a general molecular design platform that produces next-generation receptors or tectons with high affinity for Au(III) or closely related precious metal square planar coordination complexes for use in advanced materials, nanotechnology, or medicine.[4] [11] [12] [13]

Experimental Section

Materials

All chemicals and solvents were purchased as reagent grade and used without further purification unless otherwise noted. Chloroauric acid was purchased from Oakwood Chemical while bromoauric acid was purchased from Strem Chemicals. Reactions were monitored by analytical thin-layer chromatography (TLC) on silica gel 60-F254 plates, visualized by ultraviolet (254, 365 nm). NMR spectra (¹H, ¹³C) were recorded on Bruker AVANCE III HD 400 MHz spectrometer at 25 °C. Chemical shift was

presented in ppm and referenced by residual solvent peak. High-resolution mass spectrometry (HRMS) was performed using a Bruker micro TOP II spectrometer. Column chromatography was performed using Biotage SNAP Ultra columns with silica gel. 1,4-Bis(aminomethyl)durene, **BAMD**, was synthesized according to a previously published procedure.^[21]

Synthesis

Compound 1

BAMD,^[21] (0.1 g, 0.52 mmol) was stirred in acetic anhydride at 80 °C overnight. The solvent was removed to yield **1** as an off-white solid (0.141 g, 99%). ¹H-NMR (400 MHz, CDCl₃/MeOD): δ 4.44 (s, 4H), 2.26 (s, 12H), 1.97 (s, 6H) ppm. ¹³C-NMR (400 MHz, CDCl₃/MeOD): δ 170.9, 133.6, 133.0, 39.0, 22.0, 15.8 ppm. HRMS (ESI): calcd for C₁₆H₂₅N₂O₂ [M+H]⁺ 277.1911, found 277.1907.

Compound 2

BAMD^[21] (0.1 g, 0.52 mmol) and triethylamine (0.11 mL, 0.78 mmol) were combined in DCM (6 mL) with stirring. Hexanoyl chloride (0.21 mL, 1.56 mmol) was then added to the flask, upon which a white precipitate formed. The reaction mixture was allowed to stir for one hour at room temperature before the solid was collected by vacuum filtration. The pure product **2** was obtained as a white solid in 69% yield (0.14 g). ¹H-NMR (400 MHz, CDCl₃): δ 5.18 (s, 2H), 4.42 (d, J = 4.5 Hz, 4H), 2.20 (s, 12H), 2.08 (t, J = 7.6 Hz, 4H), 1.62-1.40 (m, 4H), 1.28-1.17 (m, 8H), 0.81 (t, J = 6.9 Hz, 6H) ppm. ¹³C-NMR (400 MHz, CDCl₃): δ 172.9, 134.2, 133.9, 39.3, 36.7, 31.5, 25.5, 22.4, 16.4, 14.0 ppm. HRMS (ESI): calcd for C₂₄H₄₁N₂O₂[M+H]⁺ 389.3163, found 389.3166.

Compound 3

BAMD^[21] (0.4 g, 2.08 mmol) was suspended in CHCl₃ (150 mL) with triethylamine (1 mL). Boc anhydride (0.454 g, 2.08 mmol) was dissolved in CHCl₃ (50 mL) and added slowly by addition funnel. The reaction mixture was allowed to stir overnight before the solvent was removed under reduced pressure. The resulting crude residue was purified by column chromatography (SiO2, 0-10% MeOH in CHCl3) to yield an offwhite solid (40-50% yield). This intermediate compound, t-butyl (4-(aminomethyl)-2,3,5,6-tetramethylbenzyl)carbamate (1.66 g, 5.68 mmol), was dissolved in CHCl₃ (50 mL) with triethylamine (0.8 mL). Acetyl chloride (0.45 mL, 6.3 mmol) was added to the reaction flask which was then allowed to stir overnight. The solvent was removed under reduced pressure and the resulting crude solid was purified by column chromatography (SiO₂, CHCl₃) to yield **3** as a pale yellow solid (1.45 g, 76% yield). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 5.18 (s, 1H), 4.43 (s, 2H), 4.32 (s, 2H), 2.22 (s, 6H), 2.20 (s, 6H), 1.91 (s, 3H), 1.38 (s, 9H) ppm. ¹³C-NMR (400 MHz, CDCl₃): δ 169.7, 155.5, 134.4, 134.1, 134.0, 133.6, 79.4, 40.0, 39.4, 28.4, 23.1, 22.4, 16.4, 16.4 ppm. HRMS (ESI): calcd for C19H30N2O3 [M+H]⁺ 335.2203, found 335.2219.

Compound 4

Compound **3** (1.45 g) was stirred in 20% TFA in CHCl₃ (60 mL) for 2 hours before the solvent was removed. The product was partitioned between NaOH (0.1 M, 90 mL) and DCM (80 mL). The aqueous phase was washed with DCM (3 x 50 mL) then the organic phases were combined, dried over MgSO₄, and removed by evaporation to yield **4** as an off-white solid (0.96 g, 94%). ¹H-NMR (400 MHz, MeOD): δ 4.43 (s, 2H), 4.22 (s, 2H), 2.34 (s, 6H), 2.28 (s, 6H), 1.93 (s, 3H) ppm. ¹³C-NMR (400 MHz, MeOD): δ 171.6, 134.7, 134.3, 133.9, 130.5, 398.7, 37.9, 20.8, 15.2 ppm. HRMS (ESI): calcd for C₁₄H₂₃N₂O [M+H]⁺ 235.1805, found 235.1822.

Compound 5

Compound **4** (0.96 g, 4.08 mmol) was stirred in ice-cold EtOH (50 mL). Ethyl acetimidate hydrochloride (0.6 g, 4.9) was added, upon which the reaction solution became opaque. The reaction was left to stir overnight before the solvent was removed. The crude solid was resuspended in H₂O and washed with Et₂O (4 x 60 mL). The aqueous layer was removed by

FULL PAPER

evaporation to yield **5** as a white solid (1.25 g, 98%). ¹H-NMR (400 MHz, D₂O): δ 4.28 (s, 2H), 4.23 (s, 2H), 2.18 (s, 6H), 2.11 (s, 6H), 2.10 (s, 3H), 1.86 (s, 3H) ppm. ¹³C-NMR (400 MHz, MeOD): δ 171.5, 164.7, 135.1, 134.5, 134.4, 134.1, 133.8, 129.7, 129.3, 42.0, 38.7, 37.7, 20.8, 17.1, 15.3, 15.2, 15.2, 15.1 ppm. HRMS (ESI): calcd for C₁₆H₂₅N₃O [M+H]⁺ 276.2070, found 276.2061.

Gold Co-Precipitation

The organic-soluble co-precipitation experiments were performed as follows. Stock solutions were prepared of 1 or 2 (4 mM) in CHCl₃, and HAuCl₄ or HAuBr₄ (4 mM) in dibutyl carbitol. An aliquot (0.3 mL) of the receptor solution was combined with an equal volume of each gold solution in a centrifuge tube, and the solution became cloudy almost immediately. All samples were centrifuged (4500 rpm, 5 min) and the gold pellet was removed. In each case, the mass of the gold pellet indicated >85% of the gold was recovered as a co-precipitate. The water-soluble experiments were performed in the same manner except that the stock solutions of receptor **5** and HAuX₄ were prepared in H₂O. Essentially the same recovery results were obtained when the stock solutions of HAuCl₄ and **5** were prepared in HCl (0.1 M). The recovered **5**·HAuCl₄ was dispersed into water, and then reduced with excess Na₂S₂O₅ or N₂H₂ to give a black precipitate containing the gold metal.

Crystallographic Data and Refinement

Data was acquired using a Bruker APEX-II diffractometer or a Bruker PHOTON-II using a combination of ω - and ϕ -scans of 0.5°.^[42] The data were corrected for absorption and polarization effects and analyzed for space group determination.^[43] The structures were solved by dual-space methods and expanded routinely.[44] The models were refined by fullmatrix least-squares analysis of F² against all reflections.^[45] All nonhydrogen atoms were refined with anisotropic atomic displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Atomic displacement parameters for the hydrogens were tied to the equivalent isotropic displacement parameter of the atom to which they are bonded $(U_{iso}(H) = 1.5U_{eq}(C)$ for methyl, $1.2U_{eq}(C)$ for all others). Tables of positional and thermal parameter, bond lengths and angles, torsion angles and hydrogen bond contacts are in each crystallographic information file (CIF). Deposition Numbers 2017451, 2017453, 2017454, 2017457, 2017452, 2017456, and 2017455 contain these data which are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Acknowledgements

We are grateful for funding support from the NSF (CHE1708240).

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Supramolecular chemistry • Host-Guest systems • Self-assembly • Crystal Engineering • Gold

References

WILEY-VCH

- M. D. Adams, Ed., Gold Ore Processing: Project Development and Operations, Elsevier, Singapore, 2016.
- [2] M. D. Rao, K. K. Singh, C. A. Morrison, J. B. Love, RSC Adv. 2020, 10, 4300–4309.
- [3] J. Zhang, P. J. Santos, P. A. Gabrys, S. Lee, C. Liu, R. J. Macfarlane, J. Am. Chem. Soc. 2016, 138, 16228–16231.
- [4] S. Zhang, X. Zhang, Z. Su, J. Mater. Chem. B 2020, 8, 4176–4194.
- [5] Q. Wang, Z. Wang, Z. Li, J. Xiao, H. Shan, Z. Fang, L. Qi, Sci. Adv. 2017, 3, 1–9.
- [6] R. E. M. Brooner, R. A. Widenhoefer, Angew. Chem. Int. Ed. 2013, 52, 11714–11724.
- Z. Wu, Y. Du, J. Liu, Q. Yao, T. Chen, Y. Cao, H. Zhang, J.
 Xie, Angew. Chem. Int. Ed. 2019, 58, 8139–8144.
- [8] E. R. T. Tiekink, Coord. Chem. Rev. 2014, 275, 130–153.
- [9] S. Syed, *Hydrometallurgy* **2012**, *115–116*, 30–51.
- [10] J. J. M. Nelson, E. J. Schelter, *Inorg. Chem.* 2019, 58, 979–990.
- [11] C. J. Serpell, J. Cookson, D. Ozkaya, P. D. Beer, Nat. Chem. 2011, 3, 478–483.
- X. Feng, Z. Song, Y. Liu, X. Chen, X. Jin, W. Yan, C. Yang, J. Luo, X. Zhou, D. Chen, ACS Catal. 2018, 8, 10649– 10657.
- [13] T. Lazarević, A. Rilak, Ž. D. Bugarčić, *Eur. J. Med. Chem.* **2017**, *14*2, 8–31.
- [14] M. W. Hosseini, Acc. Chem. Res. 2005, 38, 313–323.
- Z. Liu, M. Frasconi, J. Lei, Z. J. Brown, Z. Zhu, D. Cao, J.
 Iehl, G. Liu, A. C. Fahrenbach, Y. Y. Botros, O. K. Farha, J.
 T. Hupp, C. A. Mirkin, J. F. Stoddart, *Nat. Commun.* 2013, *4*, 1855–1859.
- [16] Z. Liu, A. Samanta, J. Lei, J. Sun, Y. Wang, J. F. Stoddart, J. Am. Chem. Soc. 2016, 138, 11643–11653.
- [17] R. L. Lin, Y. P. Dong, M. Tang, Z. Liu, Z. Tao, J. X. Liu, *Inorg. Chem.* **2020**, *59*, 3850–3855.
- [18] L. X. Chen, M. Liu, Y. Q. Zhang, Q. J. Zhu, J. X. Liu, B. X. Zhu, Z. Tao, *Chem. Commun.* **2019**, *55*, 14271–14274.
- [19] H. Wu, L. O. Jones, Y. Wang, D. Shen, Z. Liu, L. Zhang, K. Cai, Y. Jiao, C. L. Stern, G. C. Schatz, J. F. Stoddart, ACS Appl. Mater. Interfaces 2020, DOI 10.1021/acsami.0c09673.
- [20] C. Dong, J. Xiang, L. Xu, H. Gong, *Tetrahedron Lett.* 2018, 59, 264–267.
- [21] W. Liu, A. G. Oliver, B. D. Smith, *J. Am. Chem. Soc.* **2018**, 140, 6810–6813. This study included calculations that showed the four methyl groups on the durene ring increase π -electron density and enhance electrostatic interaction with the electropositive Au atom. The methyl CH residues also provide a periphery of partial positive charge for electrostatic interaction with the X ligands of AuX₄⁻.
- [22] The attractive electrostatic interaction between the Au center and aromatic surface is not a classic metal cation-π interaction because the four X ligands are covalently bonded to the Au center. See: K. Theilacker, H. B. Schlegel, M. Kaupp, P. Schwerdtfeger, *Inorg. Chem.* 2015,

FULL PAPER

54, 9869-9875.

- [23] E. R. T. Tiekink, J. Zukerman-Schpector, *CrystEngComm* **2009**, *11*, 1176–1186.
- [24] J. S. Hart, S. Parsons, J. B. Love, Dalt. Trans. 2011, 40, 12025–12027.
- [25] B. H. Jung, Y. Y. Park, J. W. An, S. J. Kim, T. Tran, M. J. Kim, *Hydrometallurgy* **2009**, 95, 262–266.
- [26] The noncovalent interactions within each gold complex were investigated by Independent Gradient Model (IGM) analysis (see Supporting Information). In all cases, there are large-area van der Waals binding surfaces sitting above and below the AuX₄⁻. Several polar attraction sites are distributed among these binding surfaces, stabilizing the complexes with multiple Au···π, amidinium-π···XAu, NH···XAu and CH···XAu interactions. For more information on IGD analysis, see: C. Lefebvre, G. Rubez, H. Khartabil, J. C. Boisson, J. Contreras-García, E. Hénon, *Phys. Chem. Chem. Phys.* **2017**, *19*, 17928–17936.
- [27] H. Kazama, S. Tsushima, K. Takao, *Cryst. Growth Des.* 2019, *19*, 6048–6052.
- [28] V. W. Day, M. A. Hossain, O. K. Sung, D. Powell, G. Lushington, K. Bowman-James, *J. Am. Chem. Soc.* 2007, 129, 8692–8693.
- [29] S. R. Perumalla, C. C. Sun, CrystEngComm, 2013, 15, 8941-8946.
- [30] A. R. Kennedy, N. L. C. King, I. D. H. Oswald, D. G. Rollo, R. Spiteri, A. Walls, *J. Mol. Struct.* **2018**, *1154*, 196–203.
- E. D. Doidge, L. M. M. Kinsman, Y. Ji, I. Carson, A. J. Duffy, I. A. Kordas, E. Shao, P. A. Tasker, B. T. Ngwenya, C. A. Morrison, J. B. Love, ACS Sustain. Chem. Eng. 2019, 7, 15019–15029.
- [32] E. D. Doidge, I. Carson, P. A. Tasker, R. J. Ellis, C. A. Morrison, J. B. Love, *Angew. Chem. Int. Ed.* 2016, *55*, 12436–12439.
- [33] A. S. Mahadevi, G. N. Sastry, Chem. Rev. 2016, 116, 2775–2825.
- [34] M. P. Hughes, B. D. Smith, J. Org. Chem. 1997, 62, 4492– 4499.
- [35] S. Thomas, Angew. Chem. Int. Ed. 2002, 41, 48–76.
- [36] D. Herschlag, M. M. Pinney, *Biochemistry* **2018**, *57*, 3338– 3352.
- [37] I. C. Hwang, S. W. Heo, N. J. Singh, J. W. Lee, Y. Chun, S. Bin Baek, K. S. Jin, M. Ree, H. C. Lee, S. Bin Kim, K. S. Kim, *J. Phys. Chem. B* **2010**, *114*, 7216–7221.
- [38] S. W. Heo, I. C. Hwang, Y. Chun, J. W. Lee, N. J. Singh, S. Bin Kim, K. S. Kim, *Chem. - Asian J.* 2011, *6*, 2055–2061.
- [39] L. Yang, X. Tan, Z. Wang, X. Zhang, Chem. Rev. 2015, 115, 7196–7239.
- [40] P. Anastas, N. Eghbali, *Chem. Soc. Rev.* 2010, 39, 301–312.
- [41] H. T. Chifotides, K. R. Dunbar, Acc. Chem. Res. 2013, 46, 894–906.
- [42] APEX-3. Bruker ASX. Madison, Wisconsin, USA. 2016.
- [43] L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, J.

Appl. Crystallogr. 2015, 48, 3–10.

- [44] G. M. Sheldrick, Acta Crystallogr. Sect. A Found. Crystallogr. 2015, 71, 3–8.
- [45] G. M. Sheldrick, Acta Crystallogr. Sect. C Struct. Chem. 2015, 71, 3–8.

FULL PAPER

FULL PAPER

Acyclic organic compounds reliably form a set of directional non-covalent interactions with $HAuX_4$ that enable gold recovery or crystal engineering of gold composites.





Cassandra C. Shaffer, Wenqi Liu, Allen G. Oliver, and Bradley D. Smith*

Page No. – Page No. Supramolecular Paradigm for Capture and Co-Precipitation of Gold(III) Coordination Complexes